HYPERFINE INTERACTION STUDIES ON RARE EARTH BINARY COMPOUNDS USING NMR AND PAC TECHNIQUES(核磁気共鳴及びPAC法による希土類二元化合物の超微細相互作用の研究)

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SUMMARY

The present D.Sc. thesis has emerged out of the eight years post-doctoral (post-Ph.D.) work done by the author on the hyperfine interactions in rare earth binary compounds using the continuous wave NMR, spin echo (pulsed NMR) and perturbed angular correlation (PAC) techniques. The interdisciplinary research work presented here embraces both the experimental and theoretical aspects of the problems investigated.

Thesis has been divided in two part: the first deals with the hyperfine interaction and nuclear relaxation studies on the ferromagnetic and antiferromagnetic EuB_6 using NMR technique, while the second presents hyperfine interaction studies on Laves phase rare-earth intermetallics ($TbAl_2$ and $HoAl_2$) using PAC technique.

Part I: A group of borides with the general formula MB_6, where M is an alkaline earth metal or a rare earth element, has a cubic structure of space group Pm3m. The metal atoms are at the cente of the unit cell, while boron atoms are arranged at the vertices of regular octahedra and these octahedra are linked to one another by boron-boron bonds. From the theoretical studies of Longuet-Higgins and Roberts and Hasegawa and Yanase, EuB_6, the subject matter of this part of the thesis, is expected to be a semiconductor, because the lattice parameter and Mossbauer effect experiments reveal that the Eu ions in EuB_6 are $2+(4f^7)$. Mercurio et al. reported megnetic and electrical properties on solid solutions $La_XEu_{1-X}B_6$, and showed an abrupt decrease of resistivity with the increase in the La content at high temperatures. They showed a change in the character of EuB_6 from ferroagnetic to antiferromagnetic with the increase in the La contents. By prepaing single crystals of EuB_6, we found

for the first time that the stoichiometric EuB_6 is not a ferromagnet but an antiferromagnet and the defects of Eu in EuB_6 make it a ferromagnet. The main purpose of the present investigation is to gain more knowledge about the electronic and magnetic structure of EuB_6 by investigating electron-nucleus interactions using NMR experiments. Experiments were performed in the temperature range 1.5–10 K and in the magnetic field range 0–23 kG.

CONCLUSIONS OF PART I

From the NMR experiments on the ferromagnetic EuB_6(which contains about 0.2% conduction electrons per Eu ion) and the antiferromagnetic EuB_6 (which contains about 2% conduction electron per Eu ion), we arrive at the following conclusions on the electrical and magnetic properties of this compound:

1. From the magnetization measurements on the single crystals of EuB_6, we first found that the pure FuB_6 is not a ferromagnet but an antiferromagnet.
2. Core polarization in EuB_6 is numerically largest amongst the various Eu compounds. If there exists covalent bonding between B and Eu, it may be between B p and Eu 5d orbitals
3. From the theoretical point of view and also from the experiments related to H_1 in the antiferro-magnetic EuB_6 the transferred hyperfine field in the antiferromagnetic EuB_6 is about 9 KG.
4. From the experiments on B in the ferromagnetic EuB_6, we conclude that the hyperfine field on B is −8.14kG. The field due to the conduction-electron polarization is not significant and the observed hyperfine field is due to the core polarization of 2s electrons due to the neighboring 4f shell.
5. From the T_2 measurements carried out on the antiferromagnetic EuB_6, we conclude that the Suhl-Nakamura

interaction occurs. By using this interaction, we can explain qualitatively the field dependence of the T_2 value also.

6. From the external field dependence of the spin echo intensity of the antiferromagnetic EuB_6, it is found that the ferromagnetic component of the magnetic moment is aligned to the direction of the external magnetic field above 2 kG. Below this field, antiferromagnetic domain exists.
7. The ordering temperature of the fcrromagnetic EuB_6 is about 13 K, while that of the antiferro-magnetic EuB_6 is 6.2K. Temperature dependence of the antiferromagnetic EuB_6 deviates from the brillouin function for Eu(J=7/2) to an appreciable extent.
8. A model has been suggested to account for the observed dependence of the effective field(or the local field) on the external field. Calculated results are consistent with the observed trend of the variation of the local field with the magnetic field applied externally(Fig.1)

Part II: This part deals with the experimental and theoretical sudies carried on the Laves phase compongds. After an extensive planning and taking into consideration the physical properties of rare-earth intermetallics, $TbAl_2$ and $HoAl_2$ were chosen as the suitable Laves phase compounds, which were hitherto not studied using the PAC technique. We present in this part our experimental measurements on the magnetic hyperfine field for Dy in $TbAl_2$ in the temperature range 1.5-130 K(Fig.1) Thermal equilibrium after the radioactive decay is not reached during the observation time(τ=3.1ps) and the effective field is therefore reduced. In the cubic rare earth intermetallics the main contributions to both the electric field gradient and the magnetic HF field at the nucleus come from the 4f shell and the electric field is coaxial with the magnetic field. The present experiments were carried out with the sample magnetized to saturation at right angles to the detector plane and the angular correlation was observed in the time-integral mode with the detectors set at angles 45^0, 135^0 and 225^0.

Hyperfine interactions in $Ho(Er)Al_2$ were studied using the radioactive probe of ^{166}Ho. Experiments were carried to study the effect of the cubic crystal field on the electronic levels of Er^{3+} ions in $HoAl_2$ and it was found that the crystal splitting is not significant.

CONCLUSIONS OF PART II

Main experimental and theoretical contributions of Part II to the existing literature are as follows.

1. Magnetie hyperfine field for Dy in $TbAl_2$ has been measured in the temperature range 1.5–130 K using the PAC technique. The role of electronic spin relaxation in PAC has been discussed. The relaxation time was measured between 4.2 K and room temperature and was found to be of the order of 10^{-12} s. The variation of the hyperfine field with temperature is in agreement with the trend expected from a molecular field model.
2. PAC technique has been used for the first time to study the effect of the cubic crystal field on the electronic levels of Er^{3+} ions in $HoAl_2$ and it is found that the crystal field spliting is very small. The electronic relaxation time was determined at 295 K, 80 K and 4 K and the results support a spin-spin relaxation mechanism. The hyper-fine field acting on an ^{166}Er nucleus at 4 K was obtained as 3.5±1.3 MG.
3. PAC method was applied to tow gamma-gamma cascades in ^{166}Er, one of them involving the 4^+ state and the other

6^+ state of the ground state rotational band. To obtain a high effective hyperfine field the source was taken in the from of $HoAl_2$. which forms a suitable environment for studying magnetic perturbation for states with li-fetimes in the 10^{-11} to 10^{-10} s range. $HoAl_2$ is paramagnetic above about 30 K and the experiment on both levels was performed at 50 K, where is of the order of 40, while the electronic relaxation in the 4f-shell of Er^{3+} still is fast enongh to ensure thermal equilibrium after the element transformation even for the 6^+ state. The value of g_{6+} was found to be 0.27±0.05. The gyromagnetic ratios seem to be constant to within 20% within the first three members of the rotational band.

4. Effects of co-axial magnetic and electric fields on time-integral PAC have been studied theoretically. Formulae have been developed for the angular shift in the correlation pattern and for the P factor usually measured in a four detector set-up. The formulae have been applied to all the rare earth 3^+ ions, for which values of electric and magnetic hyperfine interaction frequencies are calculated at zero temperature. The effect on the angular shift for different values of the lifetime of the excited states has been calculated for use in the interpretation of g-factor measurements at low temperatures. As an example of the temperature dependence of the hyperfine fields and angular shifts, one typical case has been calculated for the temperature region 0-150 K.
5. Effects of electron shell recovery and relaxation have been studied. The study of hyperfine interactions usually is the only way to obtain information on the electron configuration in the investigation of after-effetcs in a nuclear decay It is shown that the time-integral method for observation of the perturbation of a gamma-gamma angular correlation yields extremely valuable information on the electron shell recovery.

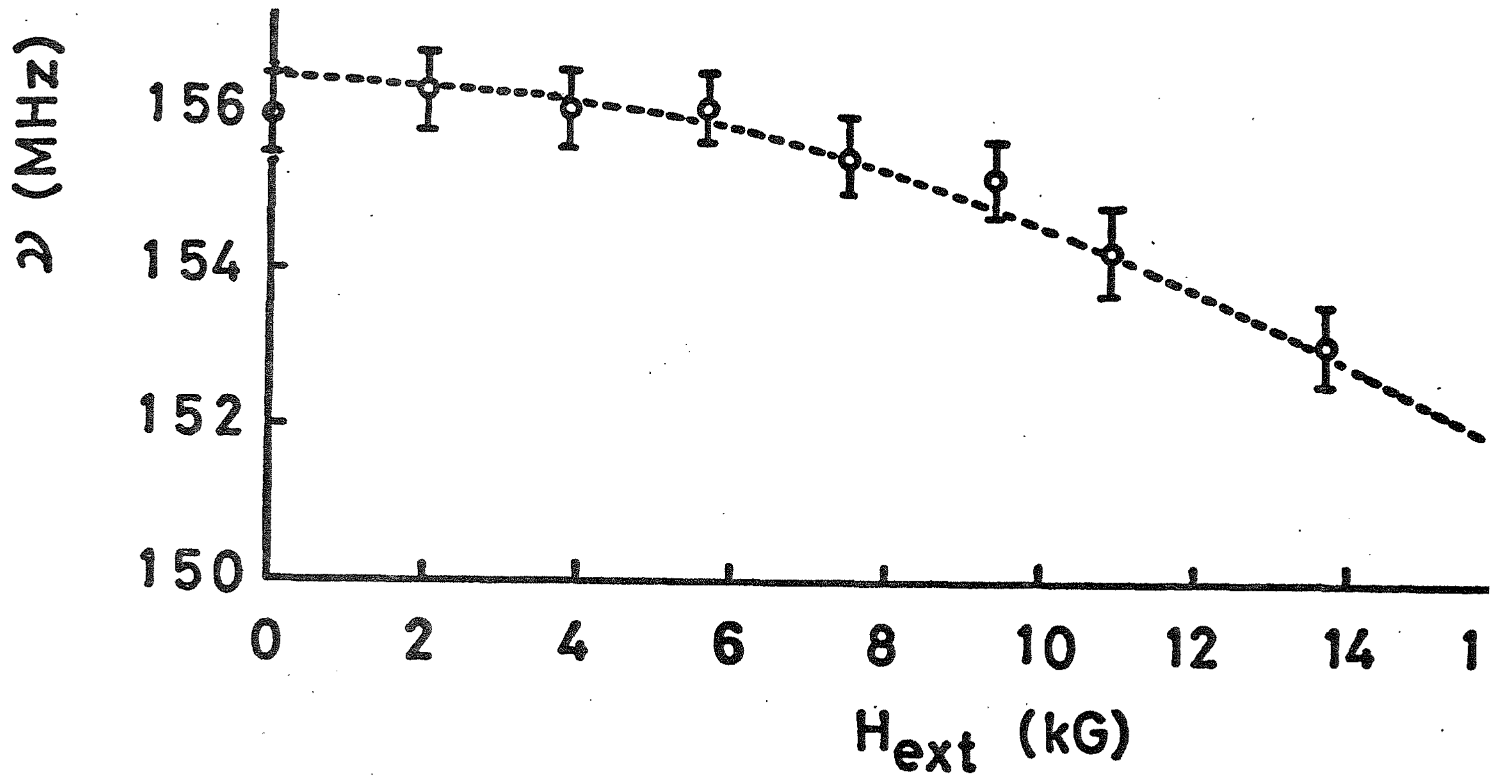

Fig. 1. Variation of the resonance frequency with the external magnetic field for the ^{153}Eu signal in the antiferromagnetic EuB_6 at 1.788 K as given by our model. Values obtained by us experimentally are also shown.

Table 1

SUMMARY OF THE RESULTS OBTAINED FOR THE TOTAL HYPERFINE FIELDS (H_{hf}) AND THE HYPFRFINE FIELDS DUE TO CONDUCTION-ELECTRON POLARIZATION (H^{e}_{hf}) FOR THE DIFFERENT SPIN ARRANGEMENTS IN THE ANTIFERROMAGNETIC EuB_6

Spin ordering	H_{hf} (kG)	H^{e}_{hf} (kG)
[110]	-346	2
[100]	-332	1.8
[111]	-341.5	6.5

Table 2

HF FIELDS AND ISOMERSHIFTS FOR FERROMAGNETIC EuB_6 & Eu-CHALCOGENIDES

Compound	H_{hf} (KG)	Isomer shift (cm/s)
EuB_6	-348	-1.31
EuO	-307	-1.19
EuS	-332	-1.25
EuSe	-330	-1.26
EuTe	-313	-1.29

論文審査の結果の要旨

EuB_6 は従来は強磁性体として知られてきたが，バジャージは共同研究者と共に純良単結晶体の作成に成功し，それが異常な反強磁性的振舞いをすることを発見した。その異常性を更に微視的立場から探究する目的を持ってバジャージは強磁性及び反強磁性的振舞いをする各種試料について主にNMRの方法を用いてあらゆる可能な測定量を測定し，次の様な知見を得た。

(i) 強磁性試料に於るNMRの各種の振舞いは大体普通の強磁性体に於る性質と似ている。

(ii) 一方，反強磁性試料に於る振舞いはかなり普通の反強磁性体と異っている。特に内部磁場の温度変化は普通よく用いられるブルリアン関数とに大きくずれている。（強磁性体ではよくこの関数に乗る）

(iii) 共鳴の巾，T_2 の磁場，温度変化は略Suhl−Nakamuraの機構で説明できる。

(iv) 2 kOe 以下の磁場では反強磁性磁区の存在がみられた。これは電気低抗のヒステレシスの存在と対応していると思われる。

(v) 内部磁場の大きさは最も良いイオン結晶と同程度であり，ボロンの固い格子形成の大きな特徴の一つと思われる。

(vi) 一部の材料では強磁性共鳴と反強磁性共鳴が共存することがみられた。しかし両者に連続的に変るのではなく，かなり不連続的に一方から他方へ転移すると思われる。以上EuB_6 が従来考えられてきた様な単純な強磁性半導体ではなく，現在最大の興味を集めて研究の行なわれている電価揺動物質の一つである可能性を与え，その微視的性質に付て多くの新しい知見を得，この方面の研究に重要な寄与をなした。

以上の様にNMRは物質の微視的内部磁場の振舞いを知る上で最も有力な手段であるが，この方法の適用できない物質も多い。それらの物質に対しては相補的手段としてPAC(Perturfed Angular Correlation)の方法がある。バジャージは各種稀土類磁性化合物に於てこのPAC法の適用可能性に付ても多くの重要な研究をなしており，この方面の研究に大きな寄与をなした。

以上バジャージは主に物質の内部磁場測定の方法を用いて稀土類磁性化合物の物性，特にその微視的機構の研究を行ない，この方面の研究に重要な寄与をなした。よってバジャージ提出の論文は理学博士の学位論文として合格と認める。